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$(Bi,Sb)_2(Te,Se)_3$-based thin film thermoelectric generators

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Abstract

Microwatt power at relatively high voltage (order of volt) was produced by $(Bi,Sb)_2(Te,Se)_3$-based thin film thermoelectric generators (TFTEGs). The generators were composed of several layers of plate-modules. Each plate-module contained 15 p/n couples and was connected electrically in series or in parallel. Maximum output power varied with the square of the temperature difference. Output voltage and current were controlled by changing the way of electrical connection as well as the number of stacked plate-modules. The output power produced per couple and per unit temperature difference was 3.5 nW/K-couple. © 2000 Elsevier Science B.V. All rights reserved.

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A large number of studies have been reported on the $(Bi,Sb)_2(Te,Se)_3$-based thermoelectric materials and devices because of their excellent performance in thermoelectric refrigeration and power generation at room temperature. Thermoelements have been usually fabricated from sintered blocks of the materials [1]. There are, however, certain difficulties and limitations in making highly miniaturized modules because of the fragile nature of these materials. Moreover, the number of p/n couples fitting in a limited space available makes it impossible to obtain relatively high output voltage (order of volt) for power generation. To overcome these drawbacks, thermoelectric modules based on thin film technology have been studied [2,3]. Microwatt or milliwatt power level is needed for electronic applications, and it could be obtained by thin film thermoelectric generators (TFTEGs) [4–8].

In this work, the TFTEGs were carefully fabricated in a stacked form of individual plate-modules containing a predetermined p/n pattern. Their performance was investigated by varying the number of stacking layers and the way of electrical connections (in series and/or in parallel) to control the output voltage and current of the TFTEG.

$Bi_{0.5}Sb_{1.5}Te_3$ (p-type) and $Bi_2Te_{2.4}Se_{0.6}$ (n-type) films were deposited on thin glass substrates (0.15 mm thick) by the flash evaporation method, using patterning masks designed for the desired dimension and shape of p- and n-legs and their junctions. A diffusion barrier layer (300-nm thick aluminum) was also deposited between p- and n-type films at the junctions. The dimension of p- and n-legs was 20 mm $(l) \times 0.67$ mm $(w) \times 4$ μm (t) and the spacing between both legs was arranged to be 0.5 mm.

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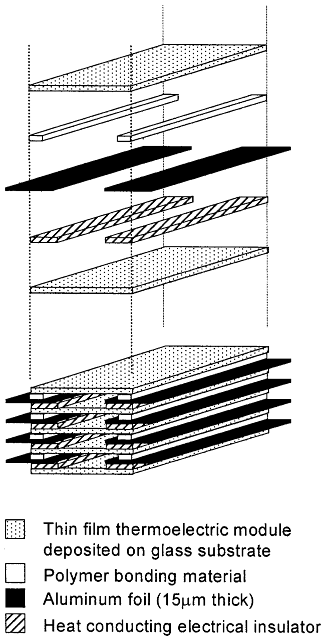

Fig. 1. Illustration for stacking procedure of the TFTEG.

Overall size of a plate-module was $40 \times 22 \times 0.15$ mm^3, which contained 15 p/n couples (Fig. 1). As shown in Fig. 2, the TFTEG was composed of several layers of the plate-modules (up to 20 layers)

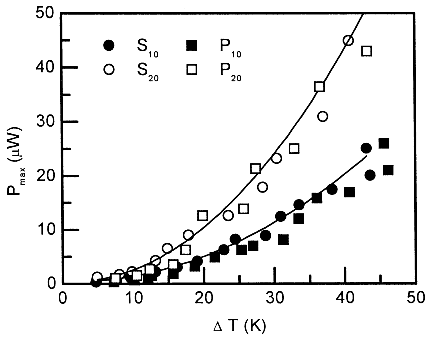

Fig. 3. Variation of maximum output power as a function of temperature difference.

that were bonded together into a stack and connected electrically in series or in parallel. Two kinds of TFTEGs are shown in Fig. 3; one is composed of 10 plate-modules while the other is composed of 20 plate-modules. Consequently, each contains 150 and 300 p/n couples, respectively. In the sample designation, S and P stand for the electrical connection of each plate-module, i.e., S for in series and P for in parallel, and the subscript after S or P indicates the number of plate-modules stacked.

Open circuit voltage (V_{OC}), short circuit current (I_{SC}), internal electric resistance (R_I) and maximum

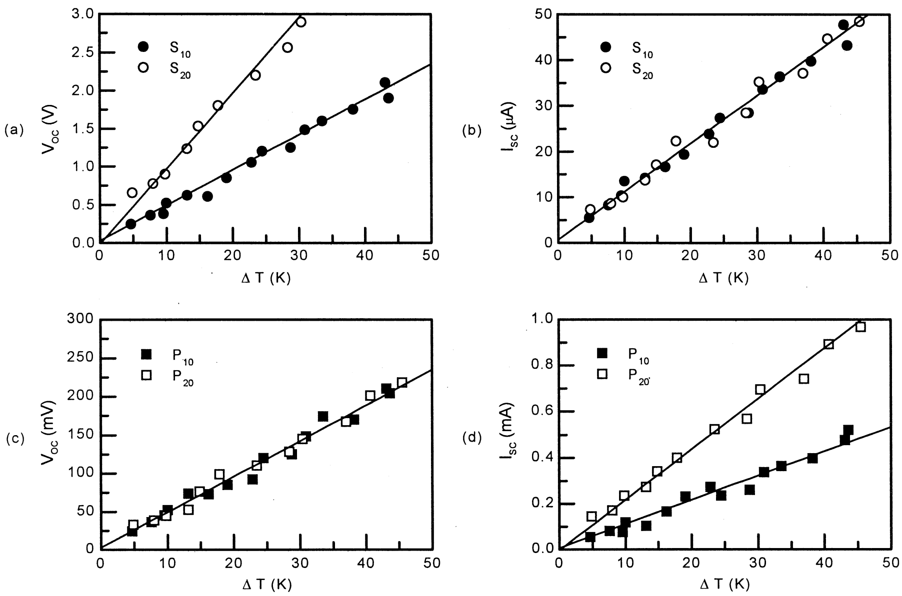

Fig. 2. Variation of open circuit voltage (V_{OC}) and short circuit current (I_{SC}) as a function of temperature difference; (a), (b) serial connection and (c), (d) parallel connection.

output power (P_{max}) were measured as a function of the number of plate-modules (N), temperature difference between hot and cold junctions (ΔT) and type of electrical connections (serial or parallel). Two parallel aluminum plates were positioned to maintain close contact with the aluminum fins attached at both hot and cold sides of the TFTEG. One of the aluminum plates is for heating by a miniature heater, and the other is for maintenance of constant temperature by circulating cold water. Temperatures of hot and cold sides were measured by T-type thermocouples attached.

If N_S and N_P plate-modules are electrically connected in series and in parallel, respectively, then, V_{OC}, I_{SC}, R_I and P_{max} can be expressed as follows: $V_{OC} = N_S V_0$, $I_{SC} = N_P V_0 / R_0$, $R_I = (N_S / N_P) R_0$ and $P_{max} = N_P N_S V_0^2 / (4 R_0)$, where V_0 and R_0 are output voltage and internal electric resistance of each plate-module, respectively.

Fig. 4 shows the variation of V_{OC} and I_{SC} as a function of N, ΔT and the way of electrical connections. As shown in Fig. 4a and c, V_{OC} varied linearly with ΔT, but for serial connection its slope depended on N, whereas there was only one slope for parallel connection, as expected from the above equations.

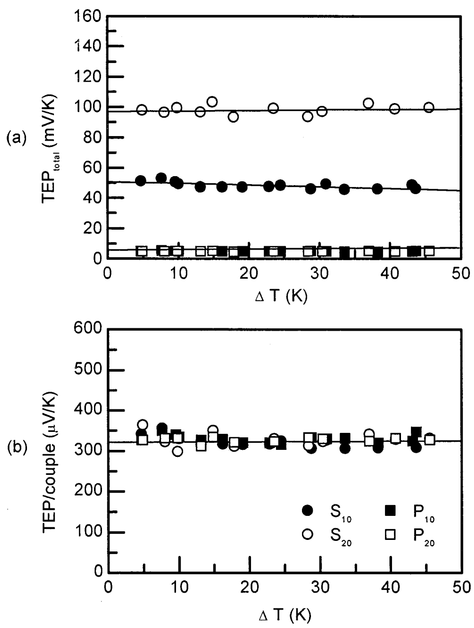

Fig. 4. Variation of (a) total thermoelectric power and (b) thermoelectric power per p/n couple against temperature difference.

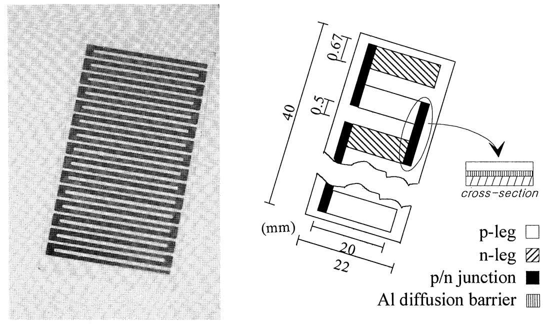

Fig. 5. Plate thermoelectric module.

This implies that there is little variation in Seebeck coefficient over the temperature ranges studied. On the other hand, I_{SC} (Fig. 4b and d) behaved oppositely to the case of V_{OC}. The variation of I_{SC} for S_{10} and S_{20} showed only one slope, however, I_{SC} for P_{10} and P_{20} had two different slopes.

For the case of serial connection, the slopes $[dV_{OC}/d(\Delta T)]$ were about 50 mV/K for S_{10} and about 100 mV/K for S_{20}, and V_{OC} reached values of an order of volt at $\Delta T \geq 10$ K for S_{20}. In this case, I_{SC} was proportional to ΔT with $[dI_{SC}/d(\Delta T)] \approx 1$ μA/K, which did not depend on N. In the parallel connection, V_{OC} was proportional to ΔT with $[dV_{OC}/d(\Delta T)] \approx 5$ mV/K. The slopes $[dI_{SC}/d(\Delta T)]$ were about 0.1 mA/K for P_{10} and about 0.2 mA/K for P_{20}. In this case, I_{SC} showed the values of an order of milliampere at $\Delta T \approx 50$ K for P_{20}.

Fig. 5 indicates the variation of P_{max} with ΔT of the TFTEG when connected in series or in parallel. Measured P_{max} varied with ΔT in a quadratic relationship as predicted from one of the aforementioned equations, and P_{max} depended linearly on N. That is, P_{max} for S_{20} or P_{20} were almost twice of S_{10} or P_{10} at a given ΔT. As presented in Fig. 6a, the total thermoelectric power (or total Seebeck coefficient) was almost constant over the temperature range studied in this experiment. It was about 50 mV/K for S_{10} and about 100 mV/K for S_{20} when connected in series, while it was only 5 mV/K for P_{10} and P_{20}, because it is independent of N when connected in parallel. Therefore, it was equal to the total thermoelectric power for one plate-module. Thermoelectric power per p/n couple, which equals to Seebeck coefficient of a p/n couple, was found to be 320 μV/K (Fig. 6b).

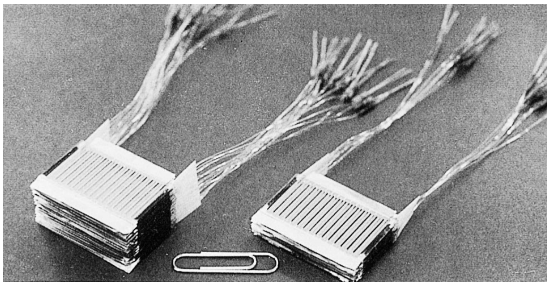

Fig. 6. TFTEGs with 20 and 10 plate-modules.

As a means for the evaluation of TFTEG performance, the reported data on a $(Bi,Sb)_2(Te,Se)_3$-based thin film battery for cardiac pacemaker [5] were compared with the results of present studies. This cardiac battery, composed of 777 p/n couples connected in series, was reported to have a total thermoelectric power of 280 mV/K (total resistance of 180 kΩ). The power produced per couple and per unit temperature difference, of S_{20} was 3.5 nW/K · couple, whereas the cardiac battery had 4.3 nW/K · couple. Reasons for the difference in output power are believed mainly due to the compositional and dimensional differences in the thermoelectric materials used. The compositions of the cardiac battery were $Bi_{0.645}Sb_{1.355}Te_{3.7}$ (p-type) and $Bi_2Te_{2.5}Se_{0.5}$ (n-type), and Seebeck coefficient of 360 μV/K was reported per p/n couple. The film thickness was 4.0 μm for p-leg and 2.85 μm for n-leg, respectively, while a uniform thickness of 4 μm for both p- and n-types in the present case. It is, however, instructive to find similar values of output power (about 4 nW/K · couple) for both cases.

In summary, TFTEGs of $(Bi,Sb)_2(Te,Se)_3$-based system were fabricated and their performances were investigated. The TFTEGs produced microwatt power at relatively high voltage (order of volt), and their output voltage and current could be controlled by changing the electrical connection as well as the number of stacking plate-modules. Open circuit voltage and short circuit current showed a linear relationship with temperature difference. There were, however, some differences in variations; open circuit voltages were dependent on the number of plate-modules when connected in series, but it was not for parallel connection. Short circuit current of S_{10} and S_{20} had the same dependence of temperature difference, but slopes of P_{10} and P_{20} were different each other. Maximum output power varied with temperature difference in the square-law relation. Its value was almost doubled when the number of plate-modules increases twice; $P_{max} \propto N$ at a given ΔT.

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